Temperature And pH Affecting The Catalytic Photodegradation of 2,4-D and MCPA pesticides in Aqueous Medium*

***Kafia M. Shareef*[1], *Salah-Aldin M.A.Naman* [2] *and Sulaiman G.Muhamad*[3]**

1- College of Nurig, University of Hawler.
2- Department of Chemistry, College of education, University of Dhuk.
3-Department of Chemistry, College of Science, University of Salahaddin
e-mail:gafff2002@yahoo.com

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Abstract

The catalytic photodegradation processes of two toxic and widely used pesticides (2,4-dichlorophenoxyacetic acid and 4-chloro-2-methylphenoxyacetic acid) were studied in aqueous suspensions of different semiconductors (TiO_2, ZnO and TiO_2 +ZnO) under UV light radiation. The effect of pH on the mode of the catalytic photodegradation was followed up in the range of pH ≅ 2 to 9.2. The results show that the faster degradation is in alkaline and acidic media upon comparison with neutral TiO_2 suspension solution, while in the case of using ZnO as catalysts the rate of degradation increases with an increase in the pH of the solution. A series of experiments were carried out at different temperature ranging from 10ºC to 50ºC. The activation energies obtained in these systems are: 4.35 to7.79 KJ/ mole.

Key words: pesticides , photodegradation TiO_2 and ZnO

Introduction

Pesticides are among the most widely used chemicals in the world, and also among the most dangerous to human health. They represent an important group of materials that can enter an ecosystem as beneficial species but emerge evolve as pollutants. Pesticides are highly toxic and many nanotarget organisms can suffer harmful effects if misuse or unintended release occurs [1]. The primary transformation processes (hydrolysis, photodegradation, oxidation and biodegradation) are responsible for reducing persistence and diminishing toxicity of pesticides in the environment [2].

Contaminations of water by pesticides have been investigated in many countries (Jordan [3], Egypt[4] , Kuwait[5], USA[6] , France [7], Japan[8] and Brazil [9]). We do not find any work reported about the contamination of water in IRAQ/Kurdistan.

Chlorophenoxy herbicides such as 2, 4-D and MCPA are most extensively used in IRAQ/Kurdistan. These compounds and their metabolites are soluble in water and their stability under certain environmental conditions has made them a serious threat to natural and drinking water[10].Catalytic photodegradation offers an advanced technology for the removal of toxic organics such as pesticides from

water. pH of the suspension is an important parameter in the photodegradation taking place on semiconductor particle surface since it is related to the surface charge properties of the photocatalysts [11,12].

Temperature is a significant parameter that often influences reaction rates. In general, the temperature was found to have a minimal effect on the catalytic photodegradation process. This is because a photocatalyst is activated by the adsorption of photons, and hence its true activation energy is nil whereas its apparent activation energy is often low in the range 0-80ºC [13].

Experimental

MCPA and 2,4-D supplied by Fluka AG with the purity of 97.5% and 97.95% respectively as a powder. Titanium dioxide (Anatase) and Zinc oxide used through the present work are supplied by BDH chemicals with the purity of 96.85% and 97% respectively. Methanol was HPLC grade and purchased from Tedia Company-USA.

The photodegradation experiments were carried out at room temperature (30ºC) in a laboratory-made photoreactor (see fig.1) including a 35 ml cylindrical photochemical cell.20ml of solution (50 mg/L of pesticide in distilled water) was added to the photochemical cell then irradiated immediately by 100-Hg UV lamp (230V, 50Hz and 1 Am) without selector from Osram- Germany). For catalytic photodegradation ,TiO_2 and/or ZnO are used as photocatalysts. Semiconductor powder 0.1 g/L was added to an aqueous solution of known concentration (50 mg/L) of pesticide solution mixture. The reaction mixture was stirred magnetically in the photoreaction cell and irradiated by UV radiation.

Hitachi L-4500 diode array HPLC connected with UV-visible spectrophotometer detector and Analytical column (PRT 720041, ET2501814 Nucleosil 120-5 C18 Machereg) was used for determination of the concentration of pesticides. The conditions which used for determination of the two pesticides are *Mobile phase:* Methanol/Water (40:60 v/v) ,*Flow rate:* 1.2 ml/min ,*Detector wavelength:* 280 nm, *Injection volume*: 20μl, *Operating temperature*: 25 ºC [14].

The catalytic photodegradation process at different pH values (2,3,4,6.4,9.4) of the solutions containing 50 mg/L of pesticides and 0.1g/L of semiconductor have been studied .The pH of treated solutions were made up by using tablets from BDH Laboratory Supplies[15]. Terminal 740-pH-meter from Wellheim-Germany was used for pH measurement of the samples.

The effect of temperature on catalytic photodegradation was monitored by adjusting the temperature of circulating water between (10^o to 50^o C).The photodegradation mixture of 50mg/L of pesticides and 0.1g/L semiconductors have been used with a UV-lamp irradiation[16]. Circulating thermostat type Julabo F10-Germany was used for controlling the reaction temperature.

Results and discussion

The HPLC is a good technique to monitor the change in the concentration of 2,4-D and MCPA in water. The concentration of 2,4-D

and MCPA during the catalytic photodegradation were monitored by observing the intensity of the peaks of retention time 9.97 min for 2,4-D and 10.93 min for MCPA ,as shown in figs 2 and 3. The intensities of these two peaks decreased gradually during the degradation process.

Graphical method was employed to predict the order of the reaction. The plot of ln [pes]/[pes]° (Where, [pes] is the concentration of herbicide at time (t), [pes]° is the initial concentration of herbicide),versus irradiant time shows a straight line behavior[17]. This suggests the first-order kinetics of the catalytic photodegradation processes. The reaction rate constants (k) were determined from the slope of the straight line.

The effect of pH on the catalytic photodegradation of 2,4-D and MCPA was investigated at the pH ≅ 2,2.7,3.9,6.4 and 9.2. Figures 4 and 5 illustrate the change in reaction rate constants with the change in the initial pH for 2,4-D and MCPA solution respectively. The experiments were carried out at constant initial concentration of substrates (50 mg/L), over 0.1 g/l of catalysts (TiO_2, ZnO, TiO_2 + ZnO) and under UV irradiation.

As it can be seen in figures 4 and 5, in alkaline solutions (pH>6.5) the reaction rate constant for both pesticides and over all types of catalysts increased with an increase in the initial pH of solution, while in acidic solution (pH<6.5) and over TiO_2 catalysts, the reaction rate constant increased with a decrease in pH values, attaining a maximum values of 0.0332 min^{-1} at pH =2.7 for 2,4-D and 0.036 min^{-1} at pH 3.9 for MCPA. A further decrease in pH after the maximum point led to a decrease in the values of reaction rate constant.

In acidic solution (pH<6.5) and over ZnO and TiO_2 + ZnO catalysts, the reaction rate constant was decreased with decreasing of pH values of solution. These observations can be interpreted on the basis of the effect of pH of the solution on the surface changes of the TiO_2 and ZnO. Where TiO_2 is in contact with water, its surface becomes hydroxylated. The surface hydroxyl group could undergo protonation and deprotonation according to the following equations[18] .

$$TiOH_2^+ \longleftrightarrow TiOH + H^+ \quad ...(1)$$

$$TiOH \longleftrightarrow TiO^- + H^+ \quad .....(2)$$

The above equations show that the surface of the TiO_2 has a net positive charge at low pH and a net negative charge at high pH. The pH at which the surface has an equivalence of positive and negative charges is defined as the zero point charge (zpc), for TiO_2 and ZnO ,the pzc can be estimated by 5.2 and 8.3 respectively [19,20].

The reaction rate change with pH values over TiO_2 in acidic solution (pH <6.5) can be correlated with zpc of TiO_2 and with pKa of the 2,4-D (pKa =2.8) [21] and MCPA (pKa =3.9) [22] . For solutions of initial pH lower than the zpc of TiO_2, the positively charged surface favors the adsorption of the negatively charged species (2,4-D and MCPA anions) in solution. In the case of ZnO the decreasing of reaction rate constant with decreasing of pH values in acidic solution may be due to the dissolving of ZnO in the acidic solution [16,23].

The increasing trend of reaction rate constant with increasing pH in alkaline solution can be ascribed to the process 3 [19] .

$$OH^- + h^+ \longrightarrow {}^{\cdot}OH \quad .....(3)$$

The activation emerges (Ea) were determined by following the concentration of pesticides at 10, 20,30,40,50ºC, under UV-irradiation and over different types of catalysts, as shown in Fig. 6.At each temperature the pseudo first order degradation constant was estimated, the values of the rate constant (k)were plotted in the form lnk versus 1/T (K), as shown in Fig. 7.

The energy of activation (Ea) was determined according to Arrhenius equation (equation 4) [24].

$$\ln k = \ln A + (Ea/RT) \quad \ldots\ldots\ldots\ldots (4)$$

Where k is the apparent reaction rate constant, A is an empirical constant depending on compound and nonthermal system conditions, R is the universal gas constant (J/K, mol^{-1}) and T is the temperature (K). The determined activated energies are tabulated in Table 1.The results in this table indicate the low values of Ea. Therefore it might be considered that the heterogeneous processes in this work are generally temperature independent[13] .Other workers also determined a low activation energies for catalytic photodegradation of atrazine and 2,4-dichlorophenol [24].

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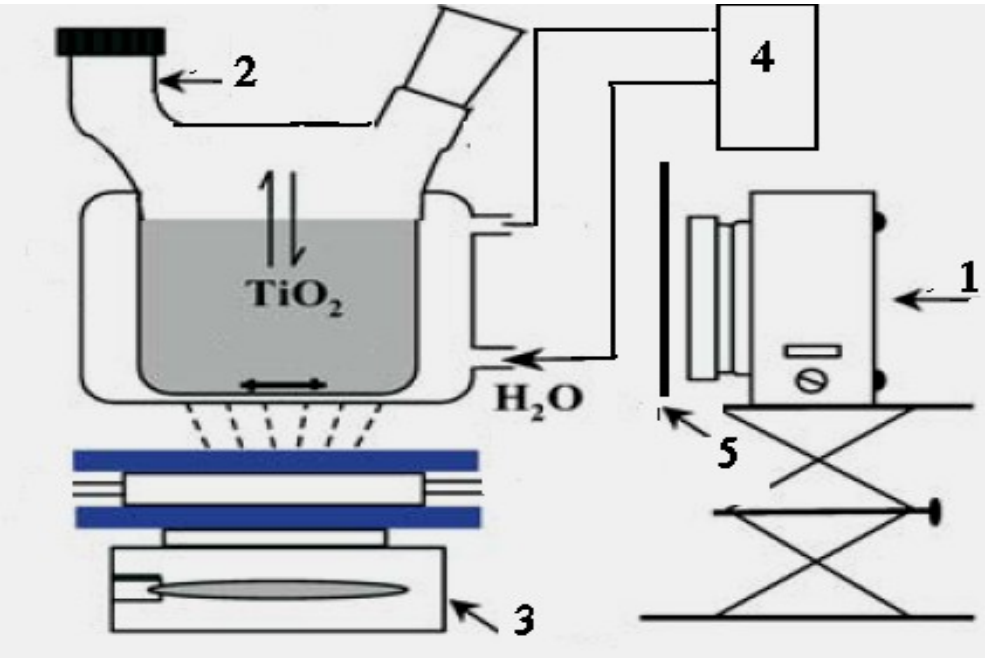

Fig.1 Block diagram of photodegradation reactor : 1-Sources of light 2-Photochemical thermostat cell 3-Stirrer 4-Recycle water bath (water circulation) 5-Line

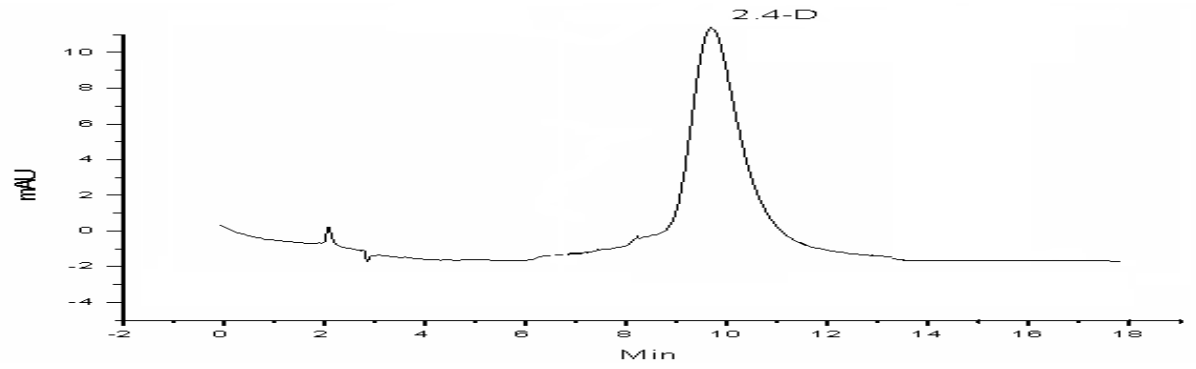

Fig. 2: HPLC chromatogram of (50 mg/L) 2,4-D

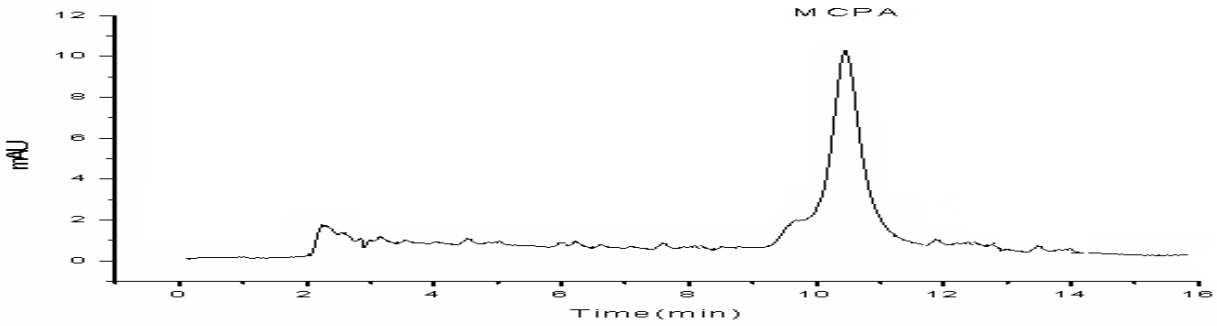

Fig. 3: HPLC chromatogram of (50 mg/L) MCPA

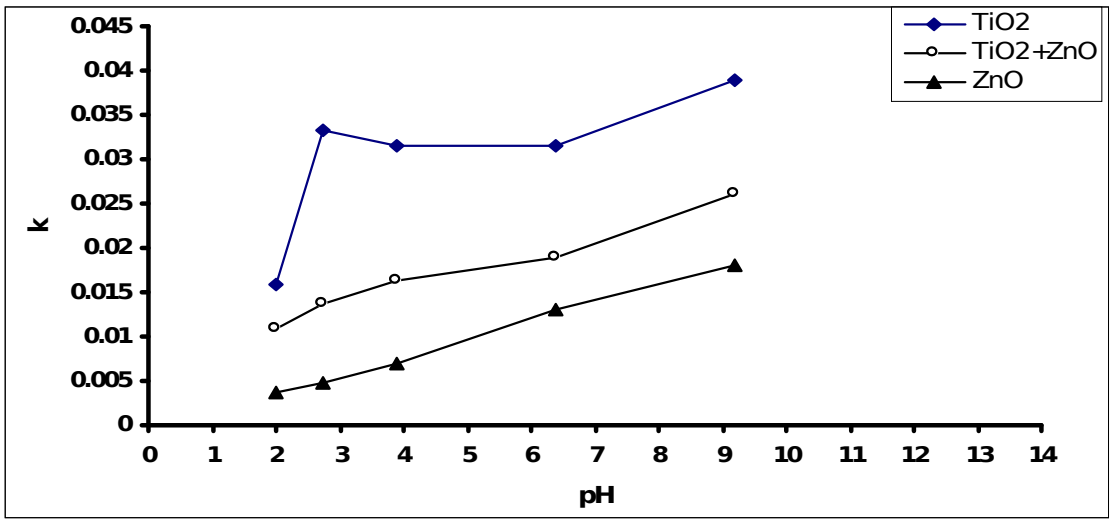

Fig.(4): Effect of initial pH on the rate of catalytic photodegradation of 2,4-D over different types of catalysts and under UV-irradiation

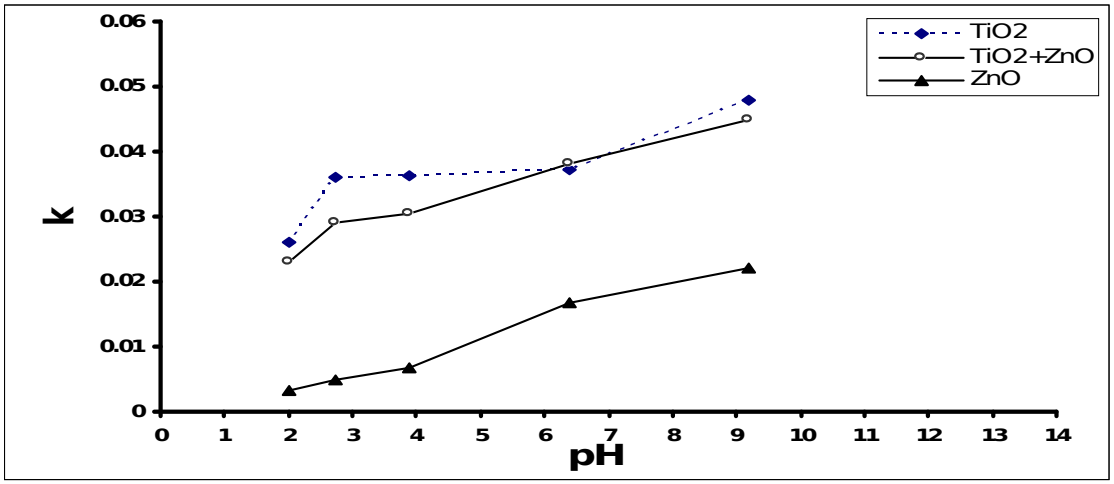

Fig.(5): Effect of initial pH on the rate of catalytic photodegradation of MCPA over different types of catalysts and under UV-irradiation

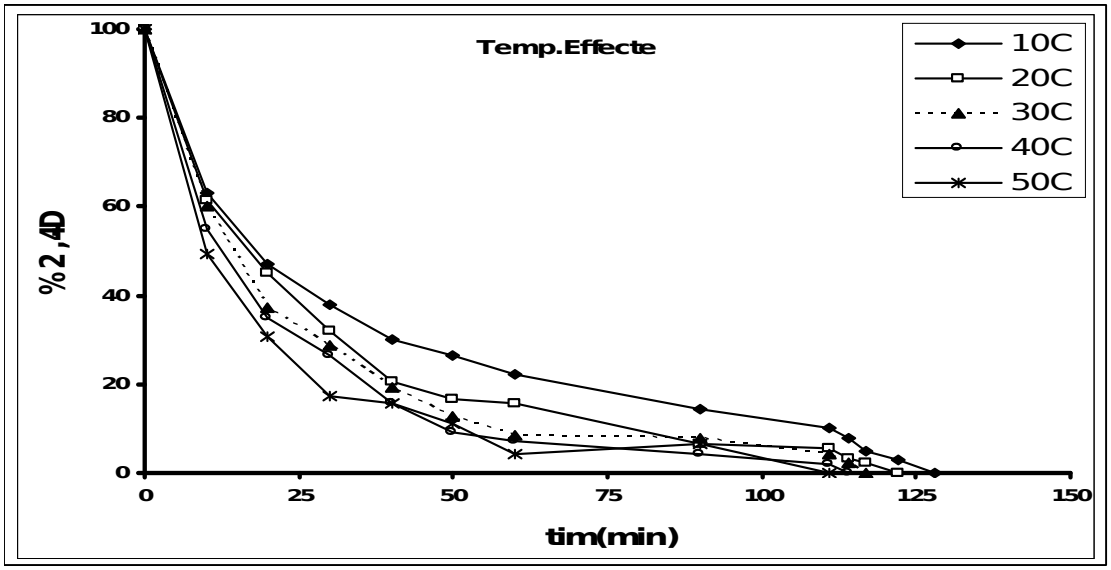

Fig. (6): 2,4-D concentration versus time at different temperature by using 50 mg/L of 2,4-D, 0.1 g/l TiO_2 and under UV-irradiation

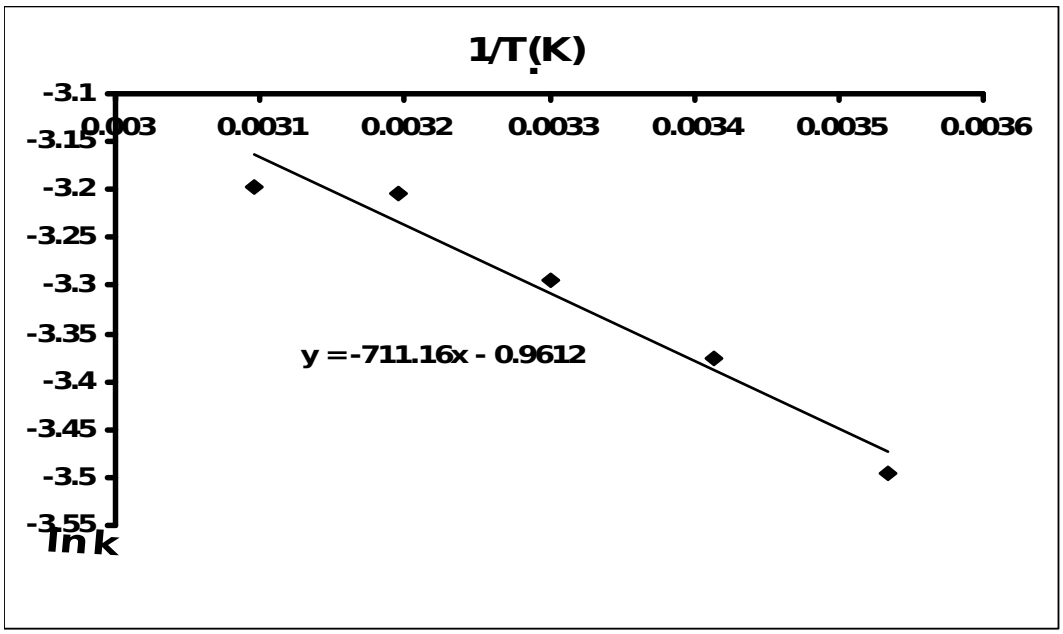

Fig. (7): ln k versus 1/T of 2,4-D degradation over TiO_2 and under UV-irradiation

Table (1): Activation energy (Ea) of 2,4-D and MCPA degradation on different catalysts and under UV irradiation

Pesticides	**2,4-D**	**MCPA**
Systems	**Ea (KJ.mol^{-1})**	**Ea (KJ.mol^{-1})**
TiO_2/UV	5.91	7.297
ZnO/UV	4.35	4.86
TiO_2 + ZnO/UV	5.50	7.76

تأثير درجة الحرارة ودالة الحامضية على عمليات التجزئة الضوئية المحفزة للمبيدين الزراعي D-2,4 و MCP في الوسط المائي

الخلاصة

عمليات التجزئة الضوئية المحفزة للمبيدين الزراعي D-2,4 و MCPA تم دراستها في وسط المائي تحت ضوء فوق البنفسجي بوجود (TiO_2, ZnO and TiO_2 +ZnO) كالعوامل المساعدة. تأثير pH على عملية التجزئة الضوئية تم دراستها في مدى مابين 2 إلى 9,2 .وجد في النتائج إن العملية التجزئة الضوئية تكون أسرع في المحيط القاعدي و ألحامضي مقارنة في المحيط المتعادل في حالة TiO_2 ولكن في حالة ZnO تزداد سرعة التفاعلات بزيادة pH المحلول.سلسلة من التجارب تمت إجرائها في دراجات حرارة مابين 10 الى 50 المئوية حيث وجدت بان طاقة التنشيط التفاعلات مابين 4,35 و 7,79 KJ/ mole .

كاريطةري ثلةى طةرمي و ترشى ناوةند لةسةر كارليَكةكانى بةتيشكة هةلَوةشانى وروذيَنراو لةسةر دوو قرِكةرى MCPA و D-2,4 لة ناوةندى ئاوى

ثوختة

كارليَكةكانى بةتيشكة هةلَوةشانى وروذيَنراو لةسةر دوو قرِكةرى MCPA و D-2,4 ئةنجامدرا لة ناوةندى ئاوى بةبكارهينانى TiO_2, ZnO and TiO_2 +ZnO وةك كاراي يَاريدةدةر و تيشكى سةروى وةنةوشيةيى .
ضونيةتى كاريطةرى pH لةسةر كارليَكةكانى بةتيشكة هةلَوةشان ليكدرايةوة لة نيوان 2 تا 9,2 و بينرا خيرايى كارليك لة ناوةندى تفت و ترشيدا خيراترة وةك ئةوةى لةناوةندى ئةمفوتيرى بيت لةكاتى بةكارهينانى TiO_2 , بةلام لةكاتى بةكارهينانى ZnO خيراى كارليك زياد دةكات بةزيادكردنى pH ى طيراوة..زنجيرةيةك تاقيكردنةوة لة ثلةى طةرمى نيوان 10 تا 50 ثلةى سةدى ئةنجامدرا و ضالاكى وزةى كارليكةكان دياريكرا لة نيوان 4,35 و 7,79 KJ/ mole